ELSEVIER Journal of Hazardous Materials 48 (1996) 137–147

JOURNAL OF HAZARDOUS MATERIALS

An NMR and XRD study of solidification/stabilization of chromium with Portland cement and β-C_2S

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Received 21 June 1995; accepted 25 October 1995

Abstract

Solidification/stabilization of chromium with Portland cement Type I and β-dicalcium silicate (β-C_2S) was investigated by means of the ^{29}Si solid state Magic Angle Spinning/Nuclear Magnetic Resonance (^{29}Si MAS/NMR) and X-ray Diffraction (XRD) techniques. It is found that chromium nitrate can increase the extent of β-C_2S hydration. It is also confirmed that the chromium ion is easily incorporated into the β-C_2S paste and hydrated Portland cement, and that it affects the characteristics of hydration and hydration products. Formation of β-calcium chromium oxide hydrate (β-$CaCrO_4 \cdot 2H_2O$) during the hydration of chromium-doped β-C_2S and calcium chromium oxide hydrate ($CaCrO_4 \cdot 2H_2O$) during the hydration of chromium-doped Portland cement indicates the substitution of chromium for silicon in hydration products. The chromium ion, Cr^{3+}, is thus stabilized and solidified through this mechanism.

Keywords: NMR; XRD; Chromium; Solidification/stabilization; β-C_2S; Cement

1. Introduction

With the implementation of the Resource Conservation and Recovery Act (RCRA), 1976, of the USA, Solidification/stabilization (S/S) processes have become essential for treating hazardous substances that are not eliminated by resource recovery, incineration and/or source reduction [1]. The S/S processes based on cement and other pozzolanic materials are being increasingly used for remediating sites contaminated by heavy metals, inorganic chemicals and organic compounds.

Many of the terminologies in the field of chemical fixation or stabilization and soilidification are borrowed from other fields. Unfortunately, such terminologies have

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SSDI 0304-3894(95)00154-9

often been used interchangeably. Originally, the term "stabilization" had collectively meant essentially pretreatment processes prior to solidification or the processes that physically change liquid or semiliquid wastes. It had also meant processes for treating sewage sludge with lime to halt biological processes and reduce odor. More recently, the US EPA has defined stabilization and solidification as follows:

Stabilization refers to techniques that reduce the hazard potential of a waste by converting the contaminants in it into least soluble, mobile, or toxic form. The physical state and handling characteristics of the waste are not necessarily changed by stabilization.

Solidification refers to techniques that encapsulate the waste in a monolithic solid of high structural integrity. The encapsulation may result in fine waste particles (micro-encapsulation) or in a large block or container of wastes (macro-encapsulation). Solidification does not necessarily involve chemical interactions between the waste and solidifying reagents, but may mechanically bind the waste into the monolith. Migration of contaminants is restricted by vastly decreasing the surface area exposed to leaching and/or by isolating the wastes within an impervious capsule.

Solidification/stabilization refers to techniques that simultaneously stabilize and solidify the waste. It is specifically cited under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA; 40 CFR 300) of the USA as a method to be considered for remediation of contaminated soils and sediments.

The complexity of an S/S process results from the combined effects of dynamic cement chemistry with solution equilibria and kinetic processes coupled with the surface and near surface phenomena. The interactions between the cement and pollutants need be determined and incorporated into detailed models of the process. Knowledge of the adsorption, precipitation, and other surface processes, however, is far from complete in dynamically reacting systems such as hydrating and setting cement [1].

There is insufficient information on: (1) the adsorption behavior of different metal cations on the surfaces of cementitious materials; (2) the chemical and physical changes taking place as a result of adsorption of these metal ions; (3) the effect of cement structure on solidification; (4) the chemical nature of the metals after S/S; and (5) the leaching behavior of different metal cations adsorbed on the surfaces of cementitious materials. To obtain such information, it requires extensive application of modern analytical techniques. It has been reported [1] that surface techniques, such as X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES) and Ion Scattering Spectroscopy (ISS), bulk characterization techniques, such as X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM), and optical spectroscopies, such as Fourier Transform Infrared (FTIR) and solid state Magic Angle Spinning/Nuclear Magnetic Resonance (MAS/NMR), can be effective in unveiling the chemistry of solidification and lead to better understanding of the mechanisms.

Solid state NMR [2] provides structural detail around selected nuclei such as Si and Al which are ideal for cement characterization. High resolution solid state ^{29}Si NMR techniques have been successfully applied to characterization of the hydration products of Portland cement [3, 4]. The chemical shift of ^{29}Si nuclei in various silica materials is dependent on the nature of the X group in Si–O–X units [5]. This chemical shift has been successfully exploited for characterizing the nature of silicate polymers in hydrated cement [6]. The orthosilicate unit SiO_4^{4-} (Q^0) in Portland cement reacts with water to give silicate polymers. The chemical shifts of the major components in hydrated cement have been designated as Q^1 for terminal SiO_3^{3-}, Q^2 for internal SiO_2^{2-}, Q^3 for branching SiO^-, and Q^4 for cross-linking unit $Si(OSi)_4$. Cartledge et al. [6] have reported that the solid state ^{29}Si NMR can serve as an effective technique in elucidating the chemistry of solidified hazardous materials. The polymerization of silicate can be effectively investigated by this technique.

In recent years, numerous studies have been carried out to investigate the mechanisms of cement hydration by the modern techniques mentioned in the preceding paragraph, especially by means of MAS/NMR which can provide useful structural information on silicon bonding [7, 8]. For example, Grimmer et al. [7] have established the correlation between the chemical shift and Si–O bond length. Tong et al. [8] have investigated the hydration of β-C_2S. Justnes et al. [9] have suggested that the degree (in term of percentage) of hydration of cement clinker (C_2S and C_3S), α, be determined by the equation,

$$\alpha = 100 - [I(Q^0)/I^0(Q^0)] \times 100 \tag{1}$$

where $I(Q^0)$ and $I^0(Q^0)$, respectively, represent the integral intensity of hydrated cement paste and cement powder at a signal of −70 ppm (Q^0). Furthermore, they have defined the average length of linear polysilicate anions in C–S–H gel, P_{Si}, as follows:

$$P_{Si} = 2[I(Q^1) + I(Q^2)]/I(Q^1) \tag{2}$$

where $I(Q^1)$ and $I(Q^2)$ are the integral intensity at −80 ppm (Q^1) and −87 ppm (Q^2), respectively. It is well known that hydration of cement silicates is a condensation process of the monomeric SiO_4^{4-} unit, Q^0, to polymeric silicates, Q^n, $n = 1$, 2, 3, 4 [10]. The ranges of ^{29}Si chemical shifts of Q^n units in solid silicates are given in Table 1.

Solidification/stabilization of heavy metals has not been investigated in depth by ^{29}Si MAS/NMR. The present study explores the mechanisms of immobilization involved in S/S of chromium with Portland cement and β-C_2S by means of this technique together with the XRD.

Table 1
Ranges of ^{29}Si chemical shifts of Q^n units in solid silicates [10]

Type	Symbol	Range (ppm)
Monosilicates	Q^0	−68 to −76
Disilicates and chain end group	Q^1	−76 to −82
Chain middle groups	Q^2	−82 to −88
Chain branching sites	Q^3	−88 to −92
Three-dimensional framework	Q^4	−92 to −129

Table 2
Chemical composition and constitution of β-C_2S and Portland cement Type I

β-Dicalcium silicate[a]		Portland cement Type I[b]	
Composition	*Weight%*	*Composition*	*Weight%*
SiO_2	33.17	SiO_2	20.38
Al_2O_3	0.26	Al_2O_3	6.77
Fe_2O_3	0.06	Fe_2O_3	3.48
CaO	63.66	CaO	64.93
MgO	0.28	MgO	0.95
SO_3	<0.01	SO_3	<0.01
Na_2O	<0.01	Na_2O	<0.01
K_2O	<0.01	K_2O	<0.01
TiO_2	0.02		
P_2O_5	0.01	*LIO*	*0.50*
Mn_2O_3	0.01	Total	99.67
SrO	0.05	*Constitute*	*Weight*
LIO	*0.87*	C_2S	20.00
Total	98.39	C_3S	51.00
		C_3A	12.10
Alkalies as Na_2O	0.02	C_4AF	10.50
Ca as $CaCO_3$	113.62	Gypsum	1.50

[a] Construction Technology Laboratories, Inc., Skokie, IL, USA.
[b] Taiwan Cement Co., Chu-Tun plant, Taiwan, ROC.

2. Materials and methods

2.1. Binding agents

The binding agents employed in this study were Portland cement Type I and β-C_2S obtained from Taiwan Cement Company, Taiwan, and Construction Technology Laboratories, Inc., Skokie, IL, USA, respectively. Their chemical compositions are listed in Table 2.

2.2. Chromium solution

A chromium solution was prepared by dissolving 200 g of compound $Cr(NO_3)_3 \cdot 9H_2O$ in 1000 g of deionized water. This compound provided the source of chromium.

2.3. Sample preparation

Samples were prepared by blending the chromium solution either with Portland cement or with β-C_2S, and stirring thoroughly until essentially homogenized. The samples were then stored in a sealed container under a relative humidity of 92% and a temperature of 25 °C for 28 d. Every sample prepared had a water-to-solid (*w*/*s*) ratio of 0.4. The S/S treatment was terminated by quenching the samples with acetone and drying under vacuum at room temperature. The dried samples were then ground into powder prior to testing.

2.4. XRD analysis

The XRD analysis was performed by a Siemens D-5000 X-ray diffractometer with CuKα radiation and 2θ scanning ranges between 10° and 80°.

2.5. ^{29}Si MAS/NMR analysis

The MAS/NMR analysis was carried out at 39.72 MHz of ^{29}Si with an MSL Bruker Solid State NMR-200 instrument. The numerical values of ^{29}Si chemical shifts are expressed relative to the external liquid tetramethylsilane (TMS).

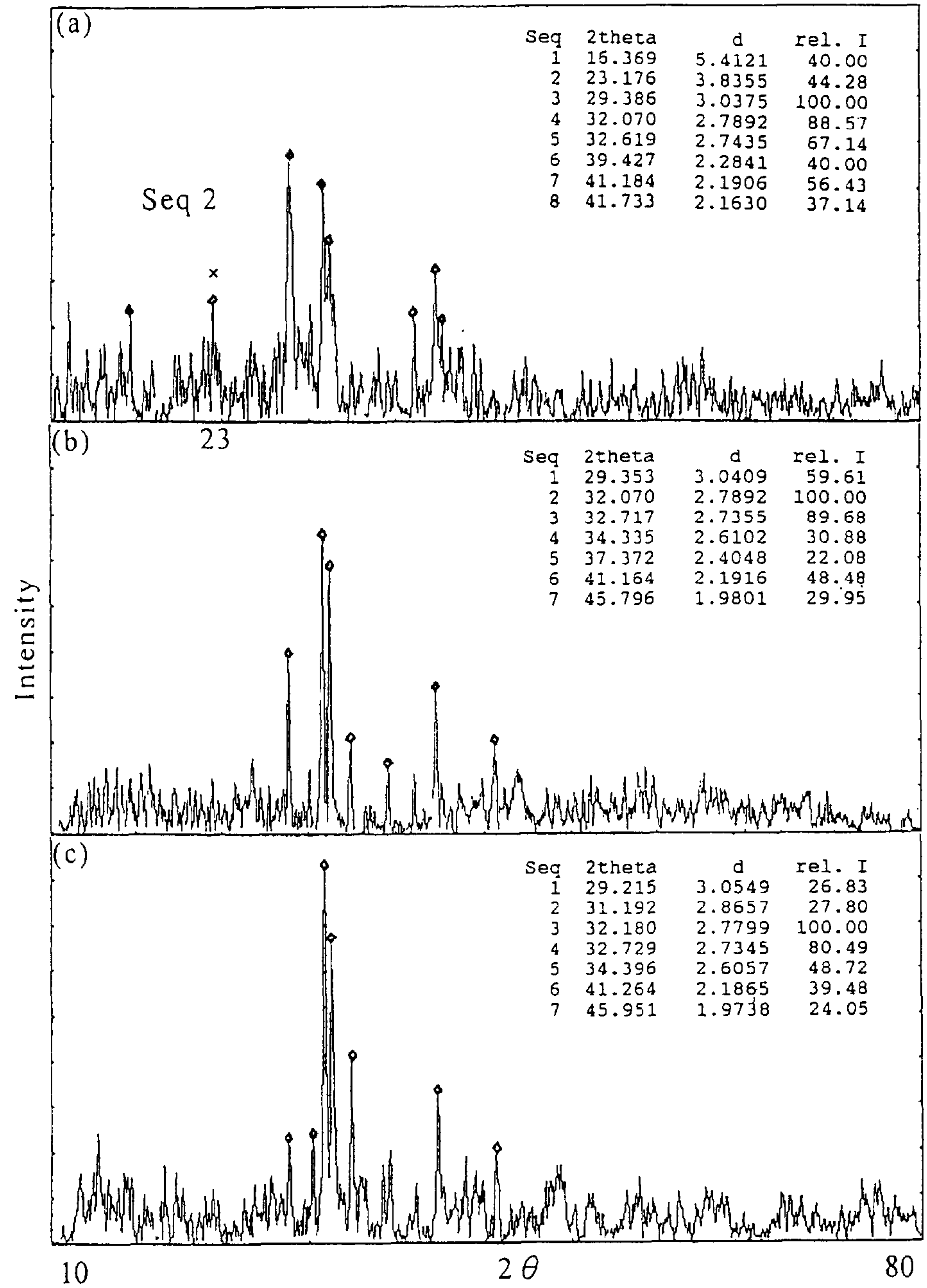
3. Results and discussion

XRD is an excellent tool to study the changes in crystallinity and appearance or disappearance of phases [11]. Any physical and chemical changes in cement caused by the addition of chromium-containing compounds can be characterized by comparing the XRD composite patterns. The Joint Committee on Powder Diffraction Standards (JCPDS) is used to identify various crystalline phases.

The XRD patterns of hydrated β-C_2S containing $Cr(NO_3)_3 \cdot 9H_2O$, hydrated β-C_2S, and pure β-C_2S samples are illustrated in Fig. 1. The appearance of β-calcium chromium oxide hydrate (β-$CaCrO_4 \cdot 2H_2O$) identified by the peak at Seq 2 ($2\theta = 23.2$) in Fig. 1(a), according to JCPDS pattern number 38-1186, indicates the substitution of chromium for silicon in calcium silicate hydrate (C–S–H) as pointed out by Mollah et al. [12]. Fig. 1(b) shows the existence of the unhydrated β-C_2S and its hydration products including calcium silicate hydrate and calcium hydroxide. The XRD pattern of pure β-C_2S sample is presented in Fig. 1(c).

Fig. 2 presents the ^{29}Si MAS/NMR spectra of hydrated samples of β-C_2S both with and without $Cr(NO_3)_3 \cdot 9H_2O$. The absorption peaks appearing at the point of -70.0 ppm for the samples with and without $Cr(NO_3)_3 \cdot 9H_2O$ indicates the existence of unhydrated β-C_2S. The hydrated β-C_2S absorption peaks mainly appear at -79.3 and -84.9 ppm; see Fig. 2(a). The hydrated β-C_2S containing $Cr(NO_3)_3 \cdot 9H_2O$ absorption peaks, however, appear at -79.4 and -85.0 ppm; see Fig. 2(b).

The XRD patterns of hydrated cement containing $Cr(NO_3)_3 \cdot 9H_2O$, hydrated cement, and unhydrated cement samples are illustrated in Fig. 3. The appearance of calcium chromium oxide hydrate ($CaCrO_4 \cdot 2H_2O$) identified by the peak at Seq 3 ($2\theta = 32.5$) in Fig. 3(a), according to JCPDS pattern number 37-1367, indicates the substitution of chromium for silicon in hydrated cement products as concluded by Ivey et al. [13]. Fig. 3(b) shows the existence of the unhydrated cement and its hydration products including calcium silicate hydrate and calcium hydroxide. The XRD pattern of Portland cement Type I sample is presented in Fig. 3(c).



(a)

Seq	2theta	d	rel. I
1	16.369	5.4121	40.00
2	23.176	3.8355	44.28
3	29.386	3.0375	100.00
4	32.070	2.7892	88.57
5	32.619	2.7435	67.14
6	39.427	2.2841	40.00
7	41.184	2.1906	56.43
8	41.733	2.1630	37.14

(b)

Seq	2theta	d	rel. I
1	29.353	3.0409	59.61
2	32.070	2.7892	100.00
3	32.717	2.7355	89.68
4	34.335	2.6102	30.88
5	37.372	2.4048	22.08
6	41.164	2.1916	48.48
7	45.796	1.9801	29.95

(c)

Seq	2theta	d	rel. I
1	29.215	3.0549	26.83
2	31.192	2.8657	27.80
3	32.180	2.7799	100.00
4	32.729	2.7345	80.49
5	34.396	2.6057	48.72
6	41.264	2.1865	39.48
7	45.951	1.9738	24.05

Fig. 1. XRD patterns of (a) hydrated β-C_2S containing $Cr(NO_3)_3 \cdot 9H_2O$, (b) hydrated β-C_2S, and (c) pure β-C_2S.

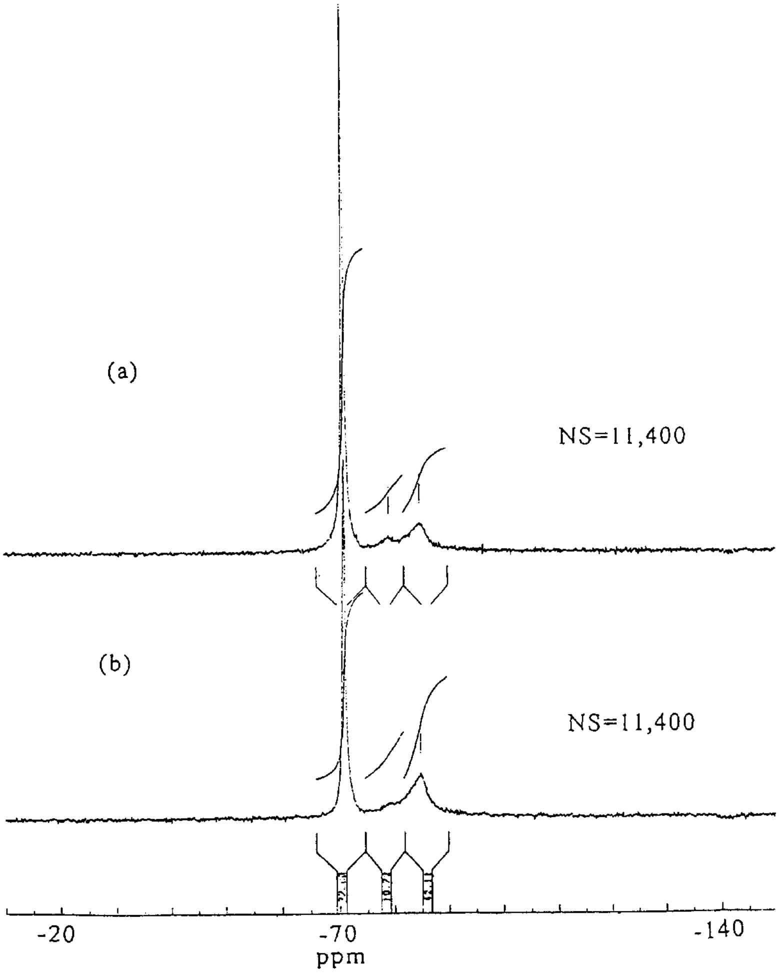
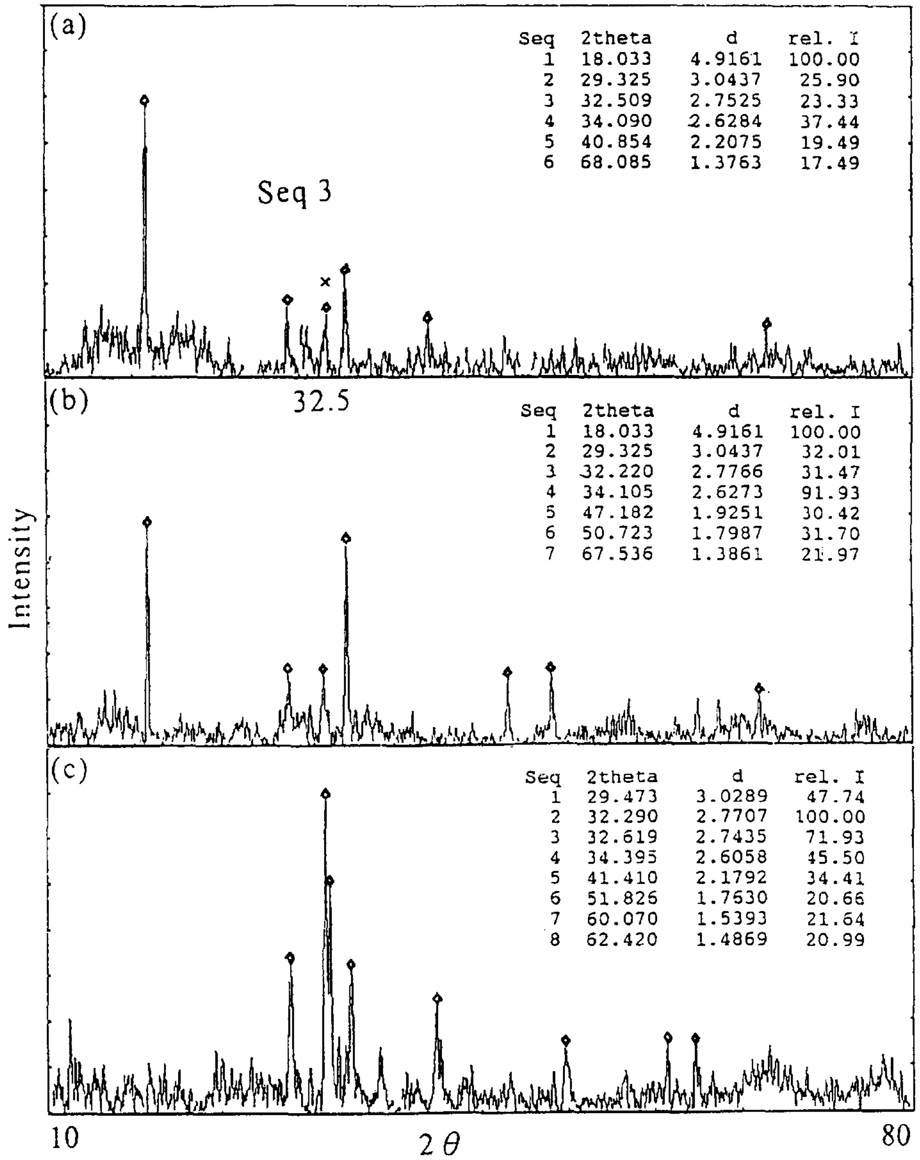


Fig. 2. ^{29}Si MAS/NMR spectra of (a) hydrated β-C_2S and (b) hydrated β-C_2S containing Cr $(NO_3)_3\cdot 9H_2O$.

Fig. 4 shows the ^{29}Si MAS/NMR spectra of hydrated samples of cement both with and without $Cr(NO_3)_3\cdot 9H_2O$. The absorption peaks appearing at the point of −70.0 ppm for the samples both with and without $Cr(NO_3)_3\cdot 9H_2O$ indicate the existence of unhydrated cement. The hydrated cement absorption peaks mainly appear at −80, −82, and −84 ppm; see Fig. 4(a). The hydrated cement containing $Cr(NO_3)_3\cdot 9H_2O$ absorption peaks, however, mainly appear at −79 and −84 ppm; see Fig. 4(b).

The integral intensities of Q^0 in hydrated and unhydrated β-C_2S, $I(Q^0)$ and $I^0(Q^0)$, are 109.9 and 152.9, respectively. The integral intensities of Q^1 and Q^2 in hydrated β-C_2S, $I(Q^1)$ and $I(Q^2)$, are 15.8 and 27.2, respectively. The degree of hydration of



(a)

Seq	2theta	d	rel. I
1	18.033	4.9161	100.00
2	29.325	3.0437	25.90
3	32.509	2.7525	23.33
4	34.090	2.6284	37.44
5	40.854	2.2075	19.49
6	68.085	1.3763	17.49

(b)

Seq	2theta	d	rel. I
1	18.033	4.9161	100.00
2	29.325	3.0437	32.01
3	32.220	2.7766	31.47
4	34.105	2.6273	91.93
5	47.182	1.9251	30.42
6	50.723	1.7987	31.70
7	67.536	1.3861	21.97

(c)

Seq	2theta	d	rel. I
1	29.473	3.0289	47.74
2	32.290	2.7707	100.00
3	32.619	2.7435	71.93
4	34.395	2.6058	45.50
5	41.410	2.1792	34.41
6	51.826	1.7530	20.66
7	60.070	1.5393	21.64
8	62.420	1.4869	20.99

Fig. 3. XRD patterns of (a) hydrated cement containing $Cr(NO_3)_3 \cdot 9H_2O$, (b) hydrated cement, and (c) pure Portland cement Type I.

β-C_2S is 28.1% according to Eq. (1). The average length of linear polysilicate anions of hydrated β-C_2S is 5.4 from Eq. (2). These results together with others are summarized in Table 3. Note that the degree of hydration, α, is higher for β-C_2S with $Cr(NO_3)_3 \cdot 9H_2O$ than without; it is 44.3% for the former and 28.1% for the latter.

Table 3

^{29}Si MAS/NMR results of the S/S of chromium with cement and β-C_2S

Material	Integral intensity of Q^n, ^{29}Si NMR						Hydration (%)	α (%)	P_{Si}
	$I(Q^0)$	$I(Q^1)$	$I(Q^2)$	$I(Q^3)$	$I(Q^4)$	$I^0(Q^0)$			
Cement powder	75.5 (100)	–	–	–	–	75.5 (100)	–	–	
Hydrated cement ($w/c=0.4$)	105.8 (26.2)	162.7 (40.3)	113.9 (28.2)	14.2 (3.5)	7.5 (1.8)	404.1 (100)	73.8	–	3.4
Hydrated cement + $Cr(NO_3)_3 \cdot 9H_2O$ ($w/s=0.4$)	66.0 (41.9)	47.0 (29.8)	37.7 (23.9)	6.9 (4.4)	0.0 (0.0)	157.6 (100)	58.1	–	3.6
Hydrated β-C_2S ($w/c=0.4$)	109.9 (71.9)	15.8 (10.3)	27.2 (17.8)	0.0 (0.0)	0.0 (0.0)	152.9 (100)	–	28.1	5.4
Hydrated β-C_2S + $Cr(NO_3)_3 \cdot 9H_2O$ ($w/s=0.4$)	77.6 (55.7)	19.7 (14.1)	42.1 (30.2)	0.0 (0.0)	0.0 (0.0)	139.4 (100)	–	44.3	6.3

Note: $\alpha = 100-[I(Q^0)/I^0(Q^0)] \times 100$; $P_{Si}=2[I(Q^1)+I(Q^2)]/I(Q^1)$; w/c = water : cement; w/s = water : solid.

However, the degree of hydration is lower for cement with $Cr(NO_3)_3 \cdot 9H_2O$ than without; it is 58.1% for the former and 73.8% for the latter. This indicates that the chromium nitrate can increase the extent of hydration of β-C_2S. It, however, decreases the extent of hydration of cement which contains 80 wt% of other compounds such as C_3S, C_3A, C_4AF and gypsum.

The average length of linear polysilicate anions is higher for hydrated β-C_2S with $Cr(NO_3)_3 \cdot 9H_2O$ than without; it is 6.3 for the former and 5.4 for the latter. This indicates that the extent of β-C_2S hydration can be increased by the addition of $Cr(NO_3)_3 \cdot 9H_2O$. Similar results are obtained for hydration of cement with and without $Cr(NO_3)_3 \cdot 9H_2O$; it is 3.6 and 3.4, respectively.

4. Conclusions

The Solidification/stabilization of chromium was performed by using Portland cement Type I and β-C_2S. Some significant findings are summarized as follows:

(1) It is confirmed that chromium ion is easily incorporated into β-C_2S paste and hydrated Type I Portland cement and that it affects the characteristics of hydration and their hydration products.

(2) β-Calcium chromium oxide hydrate (β-$CaCrO_4 \cdot 2H_2O$) is formed in the S/S of chromium with β-C_2S through the substitution of chromium for silicon in calcium silicate hydrate.

(3) Calcium chromium oxide hydrate ($CaCrO_4 \cdot 2H_2O$) is formed in the S/S of chromium with Type I Portland cement through the substitution of chromium for silicon in hydrated cement products.

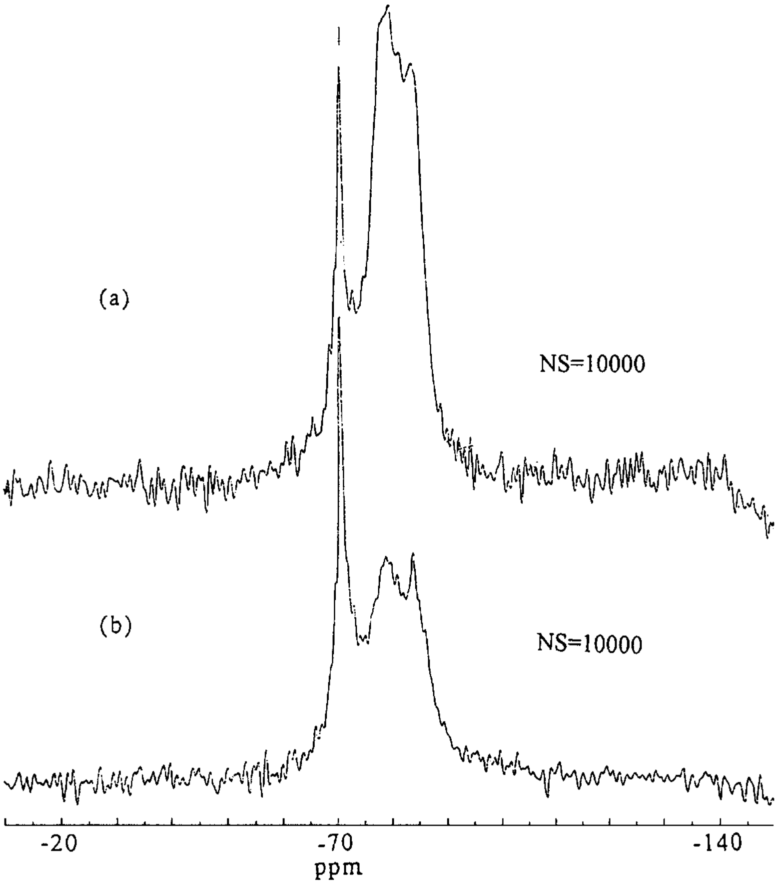


Fig. 4. ^{29}Si MAS/NMR spectra of (a) hydrated cement and (b) hydrated cement containing $Cr(NO_3)_3 \cdot 9H_2O$.

(4) Both the average length of linear polysilicate anions (P_{Si}) and the degree of hydration (α) increase in the S/S of chromium with β-C_2S containing $Cr(NO_3)_3 \cdot 9H_2O$; indicating that chromium nitrate can increase the extent of β-C_2S hydration.

Acknowledgements

This study was funded by the National Science Council of Republic of China under Contract NSC 83-0410-E-009-055.

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